

understand the fabrication, operation, and advantages offered by the present invention, including its theory of operation, and the surprising increase in the total ion current generated by the device, through reference to the detailed description which follows.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0009] **FIG. 1.** is a schematic of an exemplary electro-spray emitter array microfabricated to demonstrate a preferred embodiment of the present invention. **FIG. 1(a)** shows an array of nine electro-spray emitters arranged in a 3×3 configuration; **FIG. 1(b)** shows the dimensions for each spray emitter in the array.

[0010] **FIG. 2.** is a schematic of the experimental setups used to demonstrate a preferred embodiment of the present invention. **FIG. 2(a)** shows the experimental setup for the characterization of multielectrosprays generated from microfabricated emitter array and **FIG. 2(b)** shows the experimental setup for the mass spectrometric evaluation of the microfabricated electro-spray array.

[0011] **FIG. 3.** is a photograph of nine stable electro-sprays generated from the nine-spray emitter array.

[0012] **FIG. 4.** is a graph showing the total spray ion current vs liquid flow rate for the single electro-spray generated from a microfabricated single-spray emitter of the present invention and a fused-silica capillary for comparison using 50:50 methanol/water +1% acetic acid.

[0013] **FIGS. 5(a) and (b)** are graphs showing the total spray ion current vs total liquid flow rate for (a) multielectrosprays generated from the microfabricated emitter arrays and (b) normalized by the number of electro-sprays using 50:50 methanol/water +1% acetic acid.

[0014] **FIGS. 6(a)(b)(c) and (d)** are mass spectrometric sensitivity comparisons between (a) single electro-spray from fused-silica capillary and (b) three electro-sprays from microfabricated emitter array at flow rate of 1 $\mu\text{L}/\text{min}$, and between (c) single electro-spray from fused-silica capillary and (d) four electro-sprays from microfabricated emitter array at flow rate of 4 $\mu\text{L}/\text{min}$ with 50 $\text{pg}/\mu\text{L}$ reserpine in 50:50 methanol/water +1% acetic acid.

[0015] **FIG. 7.** is a graph showing the ESI-MS sensitivity improvement at different total liquid flow rates for a solution of 50 $\text{pg}/\mu\text{L}$ reserpine in 50:50 methanol/water+1% acetic acid multielectrosprays as the ionization source.

DETAILED DESCRIPTION OF THE INVENTION

[0016] A prototype of the present invention was fabricated on a polycarbonate substrate using a laser etching technique, and a series of experiments were conducted with the prototype, to demonstrate the use and advantages of the present invention.

[0017] While the prototype was fabricated using a polycarbonate substrate and a laser etching technique, the present invention should in no way be viewed as limited to this embodiment. Accordingly, materials and techniques commonly used for the fabrication of microscale structures should be considered as within the scope of the present invention. Exemplary techniques would therefore include,

but not limited to, laser etching, photolithographic patterning, wet chemical etching, laser ablation, plasma etching, casting, injection molding, and hot and cold stamping (embossing). Specific materials would include, but not be limited to, polycarbonate, plastic, glass, and silicon, as those materials are commonly used in the forgoing fabrication techniques. The products from these microfabrication techniques typically incorporate channels having micrometer range dimensions, and may further include valves for flow control and reservoirs for liquid storage. The use of such features also should be considered as within the contemplation of the present invention. Multiple layers of devices containing microfeatures can further be bonded together to form 3-D structures, and structures formed in this manner may be also be used to practice the present invention. While liquid flow in these structures is most often driven by the electroosmotic force induced by the electric field at the channel-liquid interface, the present invention should be understood to also include any motive force that directs liquid flow through an array of emitters, for example, pressure (e.g., using a syringe pump).

[0018] The prototype spray emitter arrays of the present invention were fabricated from a 1-mm-thick polycarbonate sheet using a laser etching method (Lumonics 848 excimer laser operating at 248 nm). **FIG. 1a** shows a prototype where an array of nine electro-spray emitters were fabricated and arranged in a three by three configuration. The emitters were positioned 1.1 mm apart, and the spray emitter tip was $\sim 150 \mu\text{m}$ in diameter with a center channel $30 \mu\text{m}$ in diameter. The center through holes were first machined by laser ablation at a high demagnification factor ($\sim 35\times$) using a small circular mask. The $450\text{-}\mu\text{m}$ -diameter and $250\text{-}\mu\text{m}$ -deep well around the each spray emitter was machined by reducing the laser beam demagnification factor to $\sim 5\times$. Because of the inherent taper of laser etching at low demagnification factors, the emitter tips produced in this way typically had a conical cross section, as illustrated in **FIG. 1b**.

[0019] To enhance the hydrophobicity of the polycarbonate surface, the surface of the microchip was treated with a CF_4 rf plasma, or coated with a Teflon thin-film by sputtering coating technology after the spray emitter array was fabricated. The increased hydrophobicity of the treated polycarbonate surface prevented the sample solution from spreading over the edge of the emitter well and afforded stable electro-sprays from each emitter.

[0020] To demonstrate multiple stable electro-sprays using these prototype microfabricated emitter arrays, the arrays were mounted to a stainless steel block using the configuration shown in **FIG. 2a**. The void behind the chip served as a liquid reservoir allowing a simultaneous supply of sample solution to each emitter. A syringe pump connected to the block through a standard LC fitting was used for sample infusion. The block assembly was mounted on an optical stand. A high-voltage dc power supply, connected to the metal block, was used to create the desired voltage difference relative to a metal counter electrode plate positioned ~ 5 mm away. An electrometer was connected to the counter electrode for measurement of total electric current of multielectrosprays, which are referred to herein as the total ion current. Upon the establishment of stable multielectrosprays, further characterization of these "chip-based" electro-sprays was also performed using this configuration. The